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Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride

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ADEQUACY OF SAMPLING TRAINS AND ANALYTICAL PROCEDURES USED FOR FLUORIDE

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Abstract—Liquid nitrogen-cooled cold-traps were used to establish the collection efficiency for fluorides of two different source sampling trains at primary aluminum reduction plants and wet-process phosphoric acid plants. It was found that the glass frit filter support commonly used in stationary source sampling trains retained fluoride during sampling; therefore, the filter should not be placed before the impingers when sampling for fluoride. Also described are the results of a collaborative test on two standard distillation procedures for fluorides: sulfuric acid distillation and steam distillation from perchloric acid. The results show that the predominant source of imprecision in both methods is the distillation step itself.

INTRODUCTION

The Environmental Protection Agency (EPA) has promulgated standards of performance for fluoride emissions from new phosphate fertilizer plants (Environmental Protection Agency, 1975) and from new aluminum reduction plants (Environmental Protection Agency, 1976). The standards require the fluoride emissions from these sources to be collected in distilled water with a Smith–Greenburg sampling train (Fig. 1). Further, they require that the samples be distilled from sulfuric acid and analyzed by either the Zirconium SPADNS analytical procedure (Method 13A) or an ion selective electrode procedure (Method 13B).

These standards are based on source testing results by the EPA. However, a study done by Leithe and Petschl (1967) questioned the collection efficiency of the EPA sampling train. So as part of our quality assurance program, we determined the quantitative collection efficiency for fluoride of the Smith–Greenburg train and a fritted-disc train similar to that used by Leithe and Petschl (Fig. 2). This was done by following the impinger sections of the sampling trains with liquid nitrogen-cooled cold-traps.

Effluents from the two plants tested represent the extremes that should be encountered in sampling for fluorides. That is, the gas stream at the phosphoric acid plant was cool (20°C), saturated (2.5% moisture),

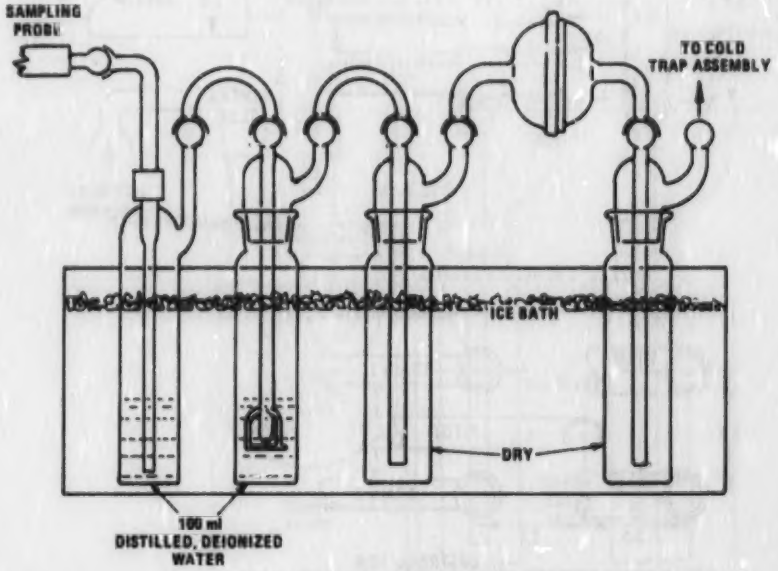

Fig. 1. Smith–Greenburg sampling train.

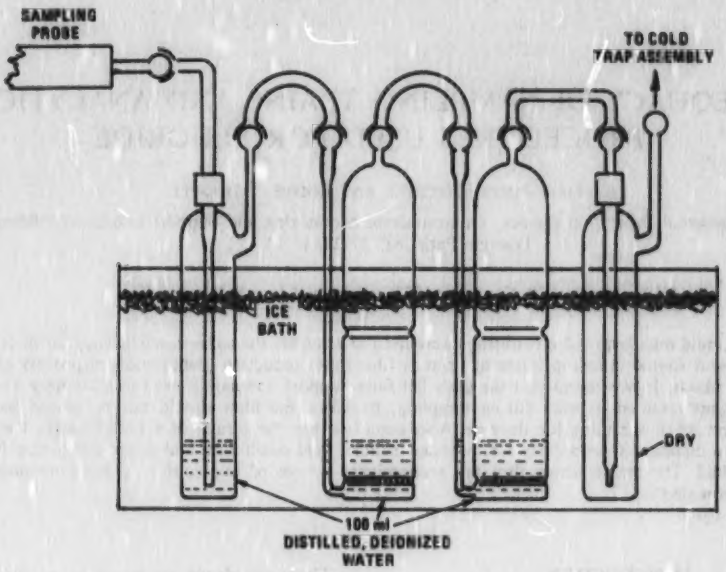

Fig. 2. Fritted-disc sampling train.

and contained high concentrations of fluorides, whereas, the gas stream at the aluminum reduction plant was hot (80°C), dry (0.3% moisture), and contained very low concentrations of fluorides.

All sampling was done isokinetically using the four probe sampling arrangement (Fig. 3) previously developed and field tested by this laboratory. It has been shown elsewhere (Mitchell, 1975) that when this sam-

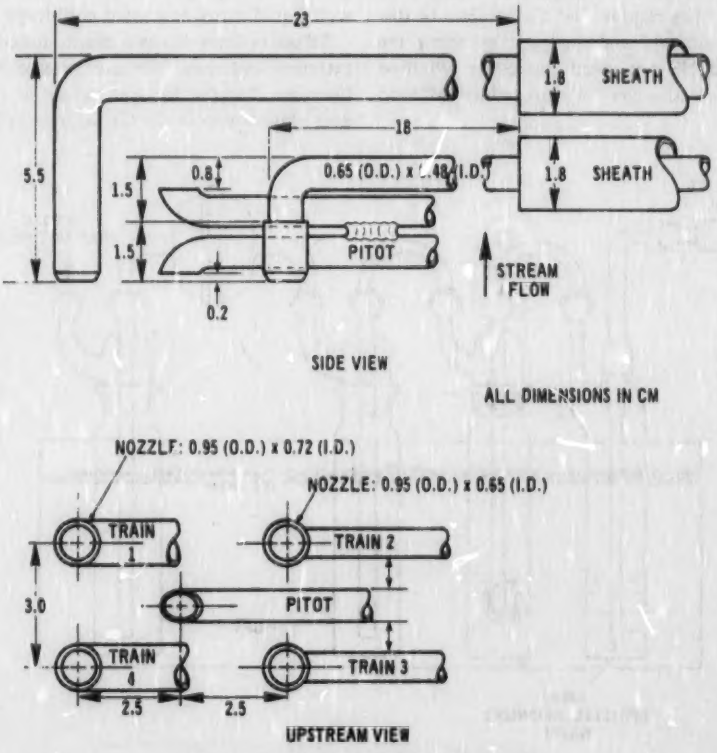

Fig. 3. Four-probe sampling arrangement.

pling probe arrangement is used, each train samples essentially the same pollutant concentration during the same run.

EXPERIMENTAL DESIGN

Wet-process phosphoric acid plant sampling

The study at this plant was done in three phases. In Phase I, the relative collection efficiencies of the two types of sampling trains were compared, that is cold-traps were not used. When an on-site fluoride analysis of the samples determined that the two types of trains had similar collection efficiencies, Phase II was initiated. In Phase II, each train was backed up with the cold-trap assembly shown in Fig. 4. This assembly cooled the sampled stack gas in the cold-trap to −110°C—a temperature sufficient to freeze out any known fluoride compound. No fluoride was found in any cold-trap, this demonstrated that both types of trains were quantitatively collecting fluoride. So, it was decided to move into the last phase of the study and determine the best precision that could be obtained at a phosphoric acid plant using the Method 13 sampling train. In this phase, the cold-traps were not used and the two fritted-disc sampling trains were replaced with Smith–Greenburg sampling trains.

Primary aluminum reduction plant

Two studies were done at the aluminum reduction plant. In the first study the relative collection efficiency of the two types of trains was evaluated using the sampling arrangement shown in Fig. 5. When the results showed that the Smith–Greenburg train consistently determined a fluoride concentration 5–10% higher than the fritted-disc train, further testing of

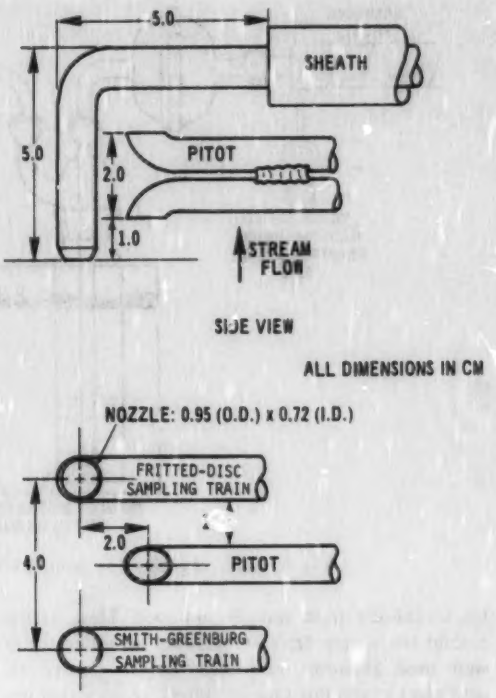

Fig. 5. Two-probe sampling arrangement.

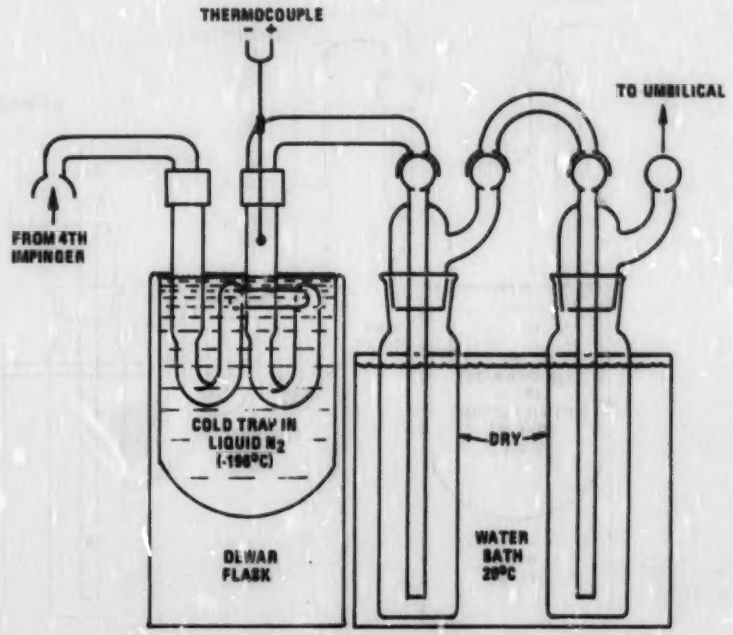

Fig. 4. Cold-trap assembly used at the wet-process phosphoric acid plant.

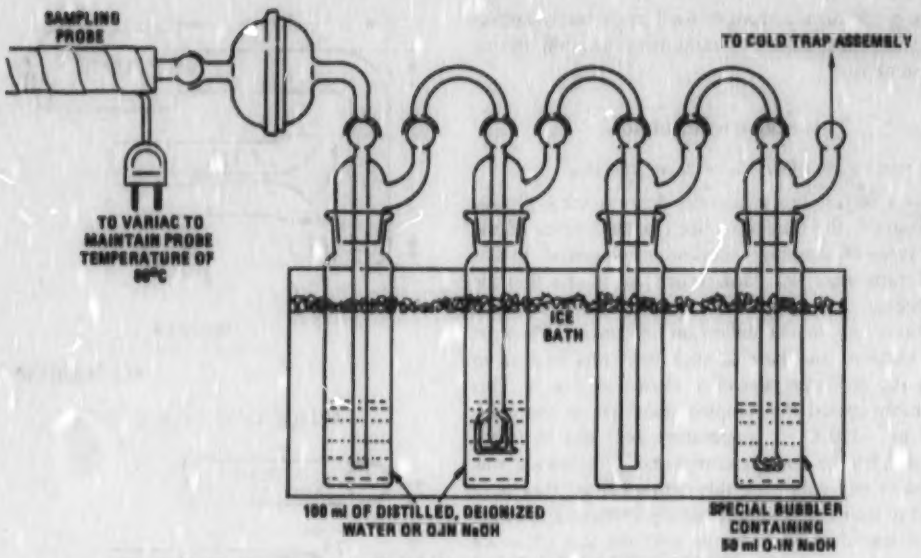
SAMPLING PROBE
TO COLD TRAP ASSEMBLY
TO VARIAC TO MAINTAIN PROBE TEMPERATURE OF 90°C
ICE BATH
100 ml OF DISTILLED, DEIONIZED WATER OR 0.1N NaOH
SPECIAL BUBBLER CONTAINING 50 ml 0.1N NaOH

Fig. 6. Smith–Greenburg sampling train as used at the aluminum reduction plant.

the fritted-disc train was discontinued. Thus, in the second study only Smith–Greenburg sampling trains were used. However, in contrast to the phosphoric acid plant study, this time the filters were located upstream of the impingers (Fig. 6) to see if the fritted-glass filter support frits would retain fluoride.

This second study had two phases. In Phase I, the collection efficiency of Smith–Greenburg trains that contained 0.1 N NaOH was compared to similar trains that contained distilled water. The primary impinger portion of each sampling train was backed up by a specially-designed bubbler that contained 50 cm^3 of 0.1 N NaOH. (The insert of this special bubbler (Fig. 6) contained a perforated (24 holes approx. 1 mm dia.), blown-glass tip to improve—relative to a standard Smith–Greenburg impinger—the contact between the impinging gas stream and the collecting liquid. In this way, we hoped to approach the collec-

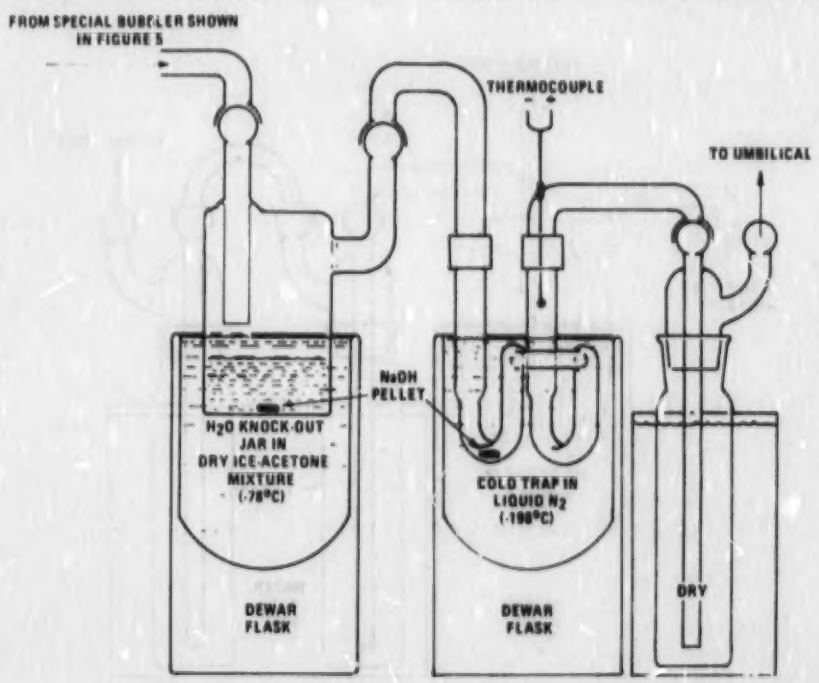

Fig. 7. Cold-trap assembly used at the aluminum reduction plant.

tion efficiency of a fritted-bubbler without actually using frits.) This bubbler was followed by the cold-trap assembly shown in Fig. 7 to cool the sampled stack gas to −130°C. This cold-trap assembly (Fig. 7) represents an improvement over that shown in Fig. 4 in that a water (ice) knock-out jar precedes the liquid nitrogen-cooled cold-trap. This addition increases the amount of gas that can be sampled (before ice plugs up the "s" shaped cold-trap) from about 1.5 to 4 m^3.

No fluoride was found in any cold-trap assembly or special bubbler, which demonstrated that both collecting liquids were quantitatively collecting fluoride. Thus, it was decided to move into the second phase of the study and determine the best sampling precision that could be obtained at an aluminum reduction plant using a Smith–Greenburg sampling train. The cold-trap assemblies were not used and only water was used in the primary portion of the trains.

SAMPLE RECOVERY AND ANALYSIS

Wet-process phosphoric acid plant samples

After each sampling run, the contents of the impingers, probes and filter holder were transferred to polypropylene sample jars. Material in the cold-trap assembly (Fig. 4) was recovered by allowing the trap to warm to room temperature while venting through 50 cm^3 of 0.1 N NaOH. Then the trap and its back-up impingers were transferred to a polypropylene jar and the trap assembly was washed with two 20-cm^3 portions of distilled deionized water and the washes placed in the jar.

After being brought to a known volume, a 10-cm^3 aliquot from each sample was mixed with 10-cm^3 of total ionic strength adjustment buffer (TISAB) and the fluoride concentration was measured with an ion selective electrode (SIE).

For the collaborative test two of the samples were filtered through Whatman 541 filter paper and then portions of the filtrates were sent, along with a laboratory-prepared standard, to six laboratories for fluoride analysis by Method 13B. In the collaborative test each laboratory first distilled an aliquot of each sample from a sulfuric acid/water solution, mixed an aliquot of the distillate with an equal volume of TISAB, and then analyze for fluoride using the SIE. Each laboratory distilled and analyzed each sample in duplicate.

For comparative purposes, these six laboratories also analyzed these samples using a procedure recommended by the Intersociety Committee (1972). In this procedure, they first steam-distilled an aliquot of the sample from perchloric acid, mixed an aliquot from the distillate with an equal volume of TISAB buffer, and then analyzed for fluoride. Again each laboratory distilled and analyzed the samples in duplicate.

After they had completed both distillation procedures and reported their results, each laboratory was told to mix an undistilled aliquot from each sample with an equal volume of TISAB and then to analyze this solution for fluoride using the SIE. This was done to determine the effect that the distillation step itself had on the precision and accuracy of the two analytical procedures.

Primary aluminum reduction plant samples

At the end of each sampling run the contents of each train from the probe up to the third impinger (Fig. 6) were placed in polyethylene bottles. Then, depending on the collecting liquid used during sampling, each train was washed with either 0.1 N NaOH or distilled, deionized water and the wash was added to the polyethylene bottle along with the filter.

The contents of the special bubbler (Fig. 6), which originally contained 50 cm^3 of 0.1 N NaOH, were placed in a 125 cm^3 polyethylene bottle. The impinger was then washed with two 20-cm^3 portions of 0.1 N NaOH, and the wash was placed in the 125 cm^3 sample bottle. The material collected in the cold-trap assembly (Fig. 7) was recovered and analyzed in a manner similar to that done at the phosphoric acid plant.

Prior to the test, the filter support frits, which had never before been used for sampling, had been soaked overnight in hot (80°C), distilled and deionized water, then oven-dried and placed in plastic bags. At the conclusion of the testing, the frits were placed in clean plastic bags and returned to the laboratory. Here they were broken into pieces and the pieces were soaked for eight hours in hot (80°C), 1.0 N NaOH to extract any fluoride collected by the frit. This extraction solution was then drained from the frit fragments, diluted to a known volume and analyzed for fluoride with the SIE. To serve as a blank, a frit that had been soaked overnight in hot, distilled, deionized water and shipped to the test site, but not used, was also extracted with hot 1.0 N NaOH and the solution was analyzed for fluoride using Method 13B.

An analysis of the samples taken in the presurvey determined that the impinger and filter samples from the aluminum plant could not be accurately analyzed without prior distillation. Thus, portions from the same train could not be distributed among different laboratories as was done with the phosphoric acid plant samples. So, the samples from each train used in sampling runs 1, 2, 6 and 7 were sent to one laboratory (Laboratory 107) for analysis by Method 13B (sulfuric acid distillation/SIE) to obtain an estimate of the within-laboratory precision of this analytical procedure on aluminum reduction plant samples. (Note! In this report, participating laboratories are identified only by randomly assigned code numbers.) To estimate the between-laboratory precision of this analytical method on aluminum plant samples, the samples from runs 3, 4 and 5 were distributed as follows among four different laboratories for analysis by Method 13B: Laboratory 108 received the samples from train 1; Laboratory 109 received the samples from train 2; Laboratory 110 received the samples

from train 3; and Laboratory 111 received the samples from train 4. Each sample was distilled and analyzed once for fluoride as required in Method 13B.

To establish an estimate for the accuracy of the analytical procedure on aluminum plant samples, a laboratory-prepared sodium fluoride solution, was included with each set of samples. To prevent the laboratories from giving special attention to this sample, however, the sample was labelled as a source sample.

RESULTS

Sampling results

The fluoride concentrations determined by each train at the phosphoric acid plant are presented in Table 1. These results are based on the analysis of undistilled samples by our laboratory. The sampling results from runs 4 and 5—runs in which all four trains were of the Method 13 design—have been used to determine the best between-train precision that would be expected if identical Method 13 sampling trains simultaneously sampled the same fluoride concentration in a stack. Three estimates are expressed as the coefficient of variation—a statistical technique that relates the within-run standard deviation to the mean fluoride concentration for that run (equation 1).

$$\%CV = \frac{\text{within-run S.D.}}{\text{run mean fluoride concentration}} \times 100. \quad (1)$$

Table 1. Sampling results from the wet-process phosphoric acid plant, mg F/scm

Phase	Sampling run	Sampling train 1	2	3	4	Run mean	% CV
I	1	27.0	26.7	23.4*	27.2*	—	—
II	2	21.9	22.8	—*,†	—*,†	—	—
	3	23.2	21.6	29.2*	17.0*	—	—
III	4	72.8	68.9	61.1	84.1	71.72	13.3
	5	94.0	77.0	70.7	75.6	79.32	12.8

* Fritted-disc trains.
† Sample lost because seam of storage bottle ruptured.

Table 2. Sampling results from the primary aluminum reduction plant, mg F/scm

Sampling run	Sampling train 1	2	3	4	Run mean	%CV
1†	0.155	0.200	0.184*	0.144*	0.171	15.1
2†	0.168	0.163	0.185*	0.187*	0.176	6.8
3‡	0.315	0.369	0.450	0.331	0.366	16.4
4‡	0.571	0.700	0.665	0.806	0.685	14.1
5‡	0.849	1.18	0.866	1.14	1.01	17.4
6†	0.277	0.315	0.362	0.339	0.323	11.2
7†	0.141	0.182	0.173	0.137	0.159	13.9

* Sampling trains in which 0.1 N NaOH was the collecting liquid.
† Samples in this run analyzed by one laboratory (Lab 107).
‡ Samples in this run distributed among four laboratories for fluoride analysis (Labs 108, 109, 110, 111).

Table 3. Interlaboratory analytical results on NaF solution containing 1.90 mg F and 200 mg of alumina

Laboratory results (mg F)*						
Lab 107	Lab 108	Lab 109	Lab 110	Lab 111	Mean	%CV
1.90	1.79	1.85	1.88	1.79	1.84	2.8

* These values have been corrected for the recovery efficiency of the distillation procedure itself.

Table 4. Analysis of filter frits from the aluminum plant

Train no.	Runs frit was used	mg F* In frit	In train	% retention†
1	1–7	0.665	7.73	8.6
2	1–7	0.249	8.89	2.8
3	1–7	0.428	7.51	5.7
4	1–3	0.366	1.98	18.5
	4–6	0.209	6.53	3.2
	7	0.109	0.48	22.6
Blank	—	0.027	—	—

* Corrected for blank of 0.027 mg found from analysis of filter frit shipped to test site but not used in sampling.
† % Retention = (total mg F in frit/total mg F in the entire train) × 100.

The fluoride concentrations determined by each train at the aluminum plant are presented in Table 2. These results, which are based on a single analysis on each sample using Method 13B, have not corrected for the amount of fluoride collected by the frit (see below).

Table 3 presents the results of a single analysis by each laboratory on the NaF standard solution that accompanied each set of aluminum plant samples. This laboratory-prepared NaF standard, which contained 1.90 mg of fluoride, a Whatman No. 1 filter, and 200 mg of alumina in 500 cm^3 of water, is representative of the ratio of alumina to fluoride being emitted by the aluminum plant.

Table 4 compares the total amount of fluoride found on the frit to the total amount of fluoride collected in the entire train (including the frit) in all the runs in which each frit was used. The last column in Table 4 shows the percentage of the fluoride collected that was retained by the filter support frit.

Collaborative test results on the phosphoric acid plant samples

Table 5 presents the individual laboratory results in mg F per liter for duplicate analyses on three aqueous fluoride solutions. Although it is standard procedure to correct fluoride distillations for the efficiency of the distillation, the procedures did not require that this correction be done. Thus, the results in Table 5 are not corrected for the efficiency of the distillation.

Table 6 presents the estimates of the precision and accuracy for a single analysis as determined from the

Table 5. Collaborative test results on the phosphoric acid plant samples

Sample no.	Analytical procedure	Laboratory results (mg F l^{-1}) 101	102	103	104	105	106	Mean	S.D. of the mean
1*	H_2SO_4/SIE	40.9	35.8	48.9	44.0	38.0	49.4	42.35	1.39
		39.9	38.8	45.6	42.5	37.5	46.9		
	$HClO_4$/SIE	44.7	57.0	47.0	56.8	46.5	46.9	47.78	2.26
		39.0	57.1	46.1	53.5	31.8	46.9		
	SIE only	39.9	43.0	43.7	42.3	41.3	43.1	42.26	0.40
		39.9	43.0	44.1	42.3	42.2	42.5		
2*	H_2SO_4/SIE	27.1	25.0	25.6	29.0	22.0	24.1	27.81	1.52
		23.3	24.3	26.6	27.3	22.0	57.5†		
	$HClO_4$/SIE	22.3	34.0	25.2	40.0	26.0	27.5	29.44	1.71
		23.8	31.0	24.7	31.8	28.2	38.8		
	SIE only	21.9	22.0	22.8	17.5	22.2	23.3	21.70	0.65
		20.3	24.0	22.8	17.5	22.4	23.7		
3‡	H_2SO_4/SIE	27.6	28.8	31.8	32.8	25.5	38.8	30.55	1.15
		27.8	30.5	31.8	29.9	§	30.8		
	$HClO_4$/SIE	28.5	45.0	29.4	40.0	31.0	46.9	36.2	2.10
		26.6	40.0	30.4	39.5	44.0	33.1		
	SIE only	27.6	30.0	30.4	29.5	29.0	29.8	29.38	0.41
		27.6	30.0	30.4	29.5	29.0	29.8		

* Source sample.
† Treated as an outlier in the statistical analysis. An estimated value was used in its place with corrections for degrees of freedom.
‡ Laboratory-prepared NaF solution that contained 29.9 mg F l^{-1}.
§ Sample exhausted before a successful distillation could be achieved.

collaborative test results reported in Table 5. Also presented in Table 6 are estimates of the precision that can be obtained if the samples are corrected for the recovery efficiency of the distillation procedure. These latter estimates, which are shown in parentheses in Table 6, were obtained by correcting each laboratory's results for the recovery efficiency it obtained on sample 3—a laboratory-prepared standard.

DISCUSSION OF RESULTS AND CONCLUSIONS

Sampling results

Because samples from two of the fritted-disc trains were lost when a seam of their storage bottles ruptured and because a third fritted-disc train sample was taken at an unacceptable isokinetic sampling rate, only three fritted-disc train samples taken at the phosphoric acid plant can be used for comparative purposes. However, since the statistical analysis determined that the results for the two types of trains were not statistically different, it is evident that the higher collection efficiency of the fritted-disc train observed by Leithe and Petschl (1967) was not observed here. Further, since fluorides were not found in any cold-trap, a collection efficiency of 100% for fluorides is assumed for both types of trains at the phosphoric acid plant.

The sampling results from runs 1 and 2 at the aluminum plant show that there was no difference in collection efficiency between those trains that used 0.1 N NaOH as the collecting medium and those that used distilled water. Since fluoride was not found in any cold-trap and since none was found in any of the special-bubblers that backed-up each sampling train (all seven runs), a collection efficiency of 100% for fluorides is assumed for the Method 13 sampling train at the aluminum plant.

The results in Table 3 and a comparison of the percentage coefficient of variation for those sampling runs analyzed by the same laboratory with those for the runs analyzed by four different laboratories (Table 2) show that the major source of the within-run variation is probably the sampling procedure and not the

Table 6. Estimates of precision and accuracy in mg F l^{-1} for a single analysis

Parameter	Entire procedure H_2SO_4/SIE	$HClO_4$/SIE	Individual steps of the procedure SIE	H_2SO_4 distillation	$HClO_4$ distillation
Within-laboratory S.D.	3.55 (3.25)*	4.89 (3.49)*	0.46	3.52	4.87
Between-laboratory S.D.	4.66 (3.25)*	7.05 (4.35)*	1.30	4.47	6.93
Accuracy† (bias)	+ 0.6	+ 6.2	−0.52	NA	NA

* Estimated precision when the results on samples 1 and 2 are corrected for the recovery efficiency of the distillation procedure.
† Based on the analysis of a laboratory-prepared NaF solution that contained 29.9 mg F/liter.

analytical procedure. Retention of fluoride by the frit is a very likely source of within-run variation, because from Table 4 it is apparent that each filter frit retained a different percentage of the total amount of fluoride collected. Further, since the fluoride concentration varied widely from run-to-run, there is no way to clearly ascertain if or when the frits became saturated with fluoride.

The phenomenon of the filter-frit retaining fluoride could explain why the fritted-disc sampling train apparently collected a lower fluoride concentration than the Smith–Greenburg train at the aluminum plant. This phenomenon may also have occurred in the fritted-disc trains used at the phosphoric acid plant, but it was not detected because of the much higher fluoride concentrations present there.

Collaborative test results

The results in Table 6 show that, when the distillation results were corrected for the recovery efficiency obtained on sample 3, the difference between the within-laboratory and the between-laboratory standard deviations decreased significantly (compared to the uncorrected distillation results). This observation infers that, when using either the H_2SO_4 or the $HClO_4$ distillation procedures for fluoride, several standard samples of known fluoride concentration should be carried through the distillation with each set of unknown samples. Further, a comparison of the precision obtained on phosphoric acid plant samples analyzed with the SIE without distillation with that obtained on duplicate samples analyzed by the SIE following distillation (Tables 5 and 6) would indicate that the distillation step should not be required if the sample contains only water soluble fluorides.

No attempt was made in this study to evaluate the SPADNS procedure (Environmental Protection Agency, 1975), because only two laboratories were found to be using this procedure and they were using it only infrequently.

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